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(54) **Composition for treating cooling systems**

(57) There is provided a composition for treating water cooling systems, the composition comprising a corrosion inhibitor such as polysilicate, a biocide such as stabilised chlorine dioxide and a flocculant, such as polyacylamide.

The combination has surprising advantages and gives a general corrosion rate of less than 5 mpy with no pitting.

The use of a flocculant in the composition of the present invention enables the stripped biofilm to be completely removed and flushed from the system.

It is believed that this combination is a careful balance which overcomes the problems of scale, deposition, corrosion and microbiological fouling and would thus be effective against legionella whilst also being environmentally acceptable.

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COMPOSITION FOR TREATING COOLING SYSTEMS

The present invention relates to the cleaning and sterilisation of industrial cooling towers, evaporative condensers and associated pipework/equipment. It also relates to the continuous treatment of such systems to prevent corrosion, scaling, deposition and microbiological contamination.

Water discharged from such systems in a controlled or adventitious manner will enter factory or site drains. It is important that the materials used are of low toxicity or their discharge could adversely affect a receiving stream.

Cooling water and its treatment still represents one of the stiffest technical challenges in industry. Arguably it is a problem which is still waiting for a final solution. There have been solutions in the past but these have been transient as further problems associated with the cooling water system have been identified or problems associated with the treatment chemicals have been discovered.

There are four problems generally associated with cooling water systems, namely corrosion, scaling, deposition and microbiological fouling. All of these

problems are interrelated.

The water treatment industry has always recognised the interrelationship between these issues but has never set out to address the overall problem. The approach has always been to attack a specific problem with a specific chemical or group of chemicals and have one or two other chemicals to either assist or to mop up the consequences. At various times in the history of cooling water treatment one of the four problems shown above has assumed a greater importance and the industry has geared itself up to finding products to deal with that specific problem. In the 1960s and 1970s the problems of scale and corrosion were identified as being much more important that the other two. The lead products were therefore corrosion inhibitors and scale control chemicals and the effectiveness of a cooling water treatment was measured in terms of how good a corrosion rate and pitting index could be achieved with minimal scaling. Good corrosion inhibitors could therefore achieve corrosion rates of < 5mpy with no pitting. These products were marketed fairly aggressively by the water treatment companies with claims that their use would minimise downtime, increase thermal efficiency and give the plant operator peace of mind.

It was recognised that cooling towers were air scrubbers and that adventitious suspended solids could get into cooling water. It was also recognised that a cooling tower provides ideal conditions for microbiological growth. Dispersants and biocides were sold by the water treatment companies in support of the corrosion/scale inhibitors but there were regarded as secondary products.

Throughout the 1970s and the early 1980s scale and corrosion inhibitors were the key products in the water treatment market place and the only real change which took place was the replacement of zinc chromate formulations by more environmentally friendly products. There are few people who would argue that zinc chromate based formulations are the best cooling water inhibitors from a price and performance viewpoint that have ever been available. The factor which led to their demise is that chromium is unacceptable in a cooling water discharge to effluent. Many water treatment companies did everything they could to sustain the use of chromate based inhibitors, eg low chrome blends and effluent treatment systems.

There are a number of lessons to be learned from this phase of cooling water treatment.

1. The water treatment industry is driven by specific problems.

2. Many of the chemicals used in cooling water systems are relatively toxic and are eventually replaced with more environmentally friendly products.

3. The industry has struggled to replace the cost efficient zinc chromate formulations.

The 1980s saw a change in the industry's approach to cooling water treatment. Once again it was specific problem driven, and it occurred almost from the moment when cooling towers became linked with Legionnaire's Disease and water was classed as a hazardous substance. As a result the emphasis switched from scale and corrosion control to that of deposition and

microbiological control. Biocides and their effectiveness particularly against Legionella become the selling focus for cooling water treatments. The interest which surrounded the whole subject of Legionella control in cooling water systems caused the entire water treatment industry to re-examine its approach.

However, while the emphasis moved and marketing changed there was a dearth of innovative products. In many instances it was simply a role reversal with biocides and dispersants being promoted and scale and corrosion inhibitors being moved back to their former position of prominence. Dispersants and in particular biodispersants became necessary to allow biocides to penetrate slime deposits in cooling water systems. (In general most conventional cooling water biocides will kill bacteria with which they come into contact. They will not penetrate biofilm).

All of the codes of practice spawned by Legionnaire's Disease favoured seasonal disinfection of cooling towers/systems. This basically means that on two occasions per annum the system is thoroughly cleaned and disinfected. Most of the procedures including HS(G)70 for carrying out these seasonal disinfections focus on the use of chlorine or chlorine based materials. As it is well known that chlorine cannot penetrate biofilm the use of biodispersants is also advocated. There are a number of lessons to be learned from this phase of cooling water treatment history.

1. During this period there was a little development of biocide products but almost no development of inhibitor/scale control formulations.

2. This phase recognised the presence of biofilm in almost every water system. The water treatment industry did not give biofilms the attention which they merit and this is still very much the case. HS(G)70 and other codes of practice do not help this. They mention the existence of biofilm but fail to address it seriously.

3. Many of the biocides which are used are fairly toxic and could not be considered as environmentally acceptable.

It may be concluded that the water treatment industry has approached cooling water treatment by reacting to whatever problem is current rather than trying to find a more universal solution or approach. The possible solutions are becoming more restricted by environmental pressures and the range of chemicals which can be used is diminishing. Many of the previous solutions, eg chromate inhibitors, and chlorophenol and tin based biocides could not be contemplated today and some of the present solutions, eg zinc and molybdenum based inhibitors and gluteraldehyde, sulphur based and quaternary ammonium compounds are becoming unacceptable due to environmental pressure. It is not inconceivable that nitrites, phosphates and some of the milder biocides will also come under environmental scrutiny in the future.

The presence of biofilm has been acknowledged and while some people in the industry have recognised its importance water treatment companies have largely ignored it.

The four major problems of cleaning water cooling systems will now be discussed in detail below:

1. CORROSION

Cooling water systems can be complex comprising an assortment of metals in a variety of configurations subjected to a wide range of different conditions (temperature, flowrate, chemical concentration). It is very probable that almost every type of corrosion mechanism will be found in a very large cooling water system (eg in a refinery or petrochemical works) during the system lifetime. The types of corrosion found in a small system may be fewer but a cross section of small systems will exhibit a full range of corrosion problems. It is surprising that water treatment companies have so few people who fully understand cooling system corrosion or who could look at a specimen and be able to give a full account of the corrosion mechanism. It is also true to state that as the large operating companies become more lean and focus on their core activities that their level of in-house expertise will reduce. Many of these companies are already almost completely reliant on their water treatment contractor and as a consequence a lot of cooling system corrosion knowledge has been lost.

There are basically two classes of corrosion, namely general wastage where the whole metal surface is affected and localised corrosion which only a small area of the metal is affected. The first class is easier to deal with; the second is more clandestine and can appear in a variety of different guises.

The prevention of corrosion in cooling water systems has been approached fairly simplistically in the past in that inhibitors which either prevent the anodic reaction or the cathodic reaction from proceeding have been used. In a new system with perfectly clean rust-

free surfaces where the water conditions do not change inhibition will be completely successful. Unfortunately these conditions rarely, if ever, exist and corrosion to some degree will occur in most systems. Metal surface condition is fundamental to corrosion protection and this is something which has rarely been taken into account by the bulk of the water treatment industry.

There are numerous accounts of disastrous attempts to introduce a corrosion inhibitor into an old system which is already exhibiting a fair degree of corrosion. The water treatment industry has always relied on laboratory evaluations to determine whether a cooling water corrosion inhibitor performs well. The tests are inevitably conducted on clean specimens under ideal conditions where changes in the physical and chemical conditions of the water are carefully controlled. In almost every cooling water system there will be some factor affecting the metal surface which will affect the performance of the corrosion inhibitor. This may be millscale which has been on the metal surface prior to commissioning, surface irregularities arising from weld spatter or poor fabrication, deposition of silt on the metal surface or the formation of a biofilm on the metal. The presence of deposits, differential temperature, differential aeration, differential concentration, crevice conditions will all thwart the most efficient cooling water inhibitor. Similarly water conditions can change markedly in a cooling system because of temperature gradients, suspended matter blowing in to the sump, adventitious leaks of product and variable concentration factor.

Cooling water inhibitors can never be fully effective and we have now appreciated that the main aim of any

cooling water treatment programme must be to give the inhibitor the maximum chance of performing well, ie the metal surface must be kept as clean as possible to maximise the ability of the inhibitor to reach the surface and protect the metal. If clean surfaces can be achieved a relatively inefficient inhibitor can offer better protection than a very efficient inhibitor will give in a system where surface deposits and biofouling obstruct the transport of the inhibitor to the surface of the metal.

In UK Patent No. 1,379,074 Petrey managed to prove that given deposit free surfaces a polysilicate-based inhibitor could perform as well as a zinc chromate-based formulation. In the 1960s Petrey tried to persuade the marketplace that it was possible to have a more environmentally friendly cooling water treatment but his ideas were never adopted commercially. Thirty years on, the environmental impact of cooling water treatment chemicals is a serious issue and arguably if a more environmentally acceptable treatment chemical is available it should be used.

2. SCALE

Scale in cooling water systems consists almost entirely of calcium carbonate and its presence can generally be predicted from the chemical analysis of the circulating water using Langelier and Ryznar Indices. Once again any predictions based on these indices are general and many unexpected scaling problems have occurred in systems operating on soft water which have experienced a small alkaline process leak in a critical exchanger. The indices also do not take into account the roughness or smoothness of the metal surface or the presence of other surface foulants, all of which can be critical to

the initial formation and keying of the scale to the metal surface.

Scale poses a number of problems in cooling water systems. These are:

1. Loss of heat transfer. This is obvious and can be critical from a process viewpoint as in general the hotter the process the greater the tendency for scale to form on the water side leading to higher process temperatures etc. This cycle ultimately leads to condenser blockage and process shutdown on high temperature.

2. Resistance to flow. In the 1960s and 1970s a lot of time and attention was given to the cost of operating cooling water systems with and without surface deposits and scale. Scale effectively reduces the diameter of the pipework increasing friction losses and pumping costs. 8% to 15% of the power costs could be saved if metal surfaces were kept clean.

3. Poor distribution. Scale can cause blockage and partial blockages resulting in insufficient water flowing to certain parts of the system. This will tend to reduce the overall efficiency of the system as there may be preferential cooling in certain areas. Linked to this there can also be scale deposits in the cooling tower itself which can block channels leading to tower inefficiency. Ultimately scale in the tower packing can lead to packing collapse.

4. Treatment Absorption. One feature of scale is its ability to absorb other treatment chemicals. This

can increase the cost of a particular treatment and render certain biocide treatments ineffective.

5. Scale harbours micro-environments. Scale in cooling water systems can be associated with corrosion deposits, adventitious deposits and biofilm. It can therefore be responsible for protecting certain bacteria from biocide treatment. It can also in certain situations lead to under deposit corrosion.

From the discussion so far it can be seen that it is not possible to control scaling in a cooling system by controlling the Langelier or Ryznar Index. The most cost efficient method of controlling scale is to use threshold treatment chemicals. These are chemicals which prevent the regular buildup of crystals and by deforming the crystal lattice prevent the formation of scale on a metal surface. The main advantage of threshold chemicals is that they are not dosed stoichiometrically and are therefore very cost efficient. We believe that threshold chemicals backed up with a chemical treatment which would keep the metal surface clean would provide the ultimate scale control programme. In general when a scale control programme is being used a corrosion inhibitor will not be required.

Once again we have now appreciated that control of scale depends to a large extent on controlling surface conditions and the key to successful scale and corrosion control must be to keep the surface of the metal clean.

3. DEPOSITION

The importance of keeping metal surfaces clean from corrosion products and scale has already been explained above. It is also clear that every attempt should be made to keep surfaces free from adventitious solids.

Suspended matter can get into the water in a cooling water system in a number of ways:

1. The cooling tower acts as an air-scrubber in which any solids present in the air will be transferred into the aqueous phase.

2. Debris left behind during the construction phase can be picked up by the water flow and perhaps transferred to a more critical part of the system.

3. Process leaks can product solid material on the water side. This would be true in situations where there is an oil or hydrocarbon leak.

4. Air borne material can enter the tower sump.

5. Algae which can form in the upper well lit areas of some large cooling water towers can fall down under its own weight contributing suspended solids to the circulating water.

The composition of material found on the metal surface of any cooling system will be extremely variable. In addition to the rust/corrosion/scale deposits likely to be found there may also be a melange of silt/sand and an assortment of organic and inorganic debris. It is almost certain that there will be some microbiological activity associated with any such deposits.

There are a number of problems associated with

deposition. Severe deposition will ultimately lead to blockage or poor distribution and as it is likely to take place in low flow areas it is important that such areas do not coincide with situations where design heat transfer conditions are critical to the process.

In general most solids in the water end up in the tower sump which effectively acts as a settlement tank.

Deposits on the metal surface can promote under deposit attack by causing differential aeration conditions on the metal surface.

It is this type of attack coupled with biofouling which can create complex conditions on the metal surfaces in cooling water systems. Deposits can provide the ideal habitat for microbiological growth in that they can often provide the food as well as the cover from biocides.

Once again a situation is produced where the metal surface and the complex interactions which take place are critical to the integrity of the system from a corrosion/scaling/deposition/microbiological viewpoint. In our view if cooling water surfaces could be cleaned and maintained in a clean condition most of the problems associated with industrial water cooling systems would disappear.

4. MICROBIOLOGICAL PROBLEMS

The understanding of the microbiology of a cooling water system has increased dramatically over the past twenty years. Arguably the most important discoveries have still to be made. Planktonic-free swimming bacteria rarely present any real problems to modern

biocide treatments and the concern today is what is happening on the various surfaces in the system. The development and maturing of biofilm on the surfaces of a cooling water system holds the key to bacterial and Legionella control in cooling systems.

The following statements are relevant:

1. Chlorine and bromine are not capable of penetrating biofilm and systems which contain a biofilm which has Legionella as part of the sessile phase and are disinfected using these biocides are capable of rapid reinfection.

2. Biofilms develop rapidly on surfaces which provide a food source. This means that elastomers and plastics will promote biofilm formation before metals, particularly copper. Obviously metal with a film of organic materials will promote biofilm formation.

3. Modern understanding of biofilm shows that it consists of a basal layer and a raised layer. The basal layer is only 5 μm thick whereas the raised layer will extend into the water flow and interact with materials dissolved or suspended in the water flow.

4. One of the main problems associated with the control of Legionella in water systems is associated with its growth within an adherent biofilm which comprises numerous other bacterial species, protozoa and ciliates. Together these form a complex balanced ecosystem in which the Legionella are able to express several physiological states; as planktonic cells, as free

living components of the biofilm ecosystem and in association with amoebae, which may become parasitised by the organism. It has been shown that the presence of iron and other nutrients will influence the type of Legionella. These factors (in particular the host, the food source, and the development of the biofilm) will all have an influence on the efficiency of any biocide treatment used to control Legionella.

It has now been appreciated that the activity at the metal surface is vital to the success of any treatment used for microbiological control in general and Legionella in particular.

New biocides capable of penetrating biofilm and killing amoeba are required.

The present invention considers all the problems faced by existing cooling water treatments in the light of some of the factors indicated in the foregoing discussion.

The criteria for a cooling water treatment programme according to the invention are:

1. The treatment must contain a constituent which will help to keep metal surfaces clean.

2. The treatment must address the problem of biofilm formation and development.

3. The materials used in the treatment must be as environmentally friendly as possible.

4. The chemicals should be easy to dose and easy to

test.

5. The treatments should be compatible with existing dosing systems and sterilisation techniques.

In the present invention a coagulant or polyelectrolyte is used to remove debris from cooling system surfaces by adding a biofilm penetrant and biocide, especially a stabilised chlorine dioxide formulation to the treatment package.

The philosophy behind the present invention is that if clean surfaces can be maintained a less efficient but also a much less toxic cooling water inhibitor is sufficient, for example polysilicate solutions to control corrosion when using polyelectrolytes and chlorine dioxide.

In addition a threshold chemical to prevent scaling and a maleic acid and phosphate copolymer may optionally be used.

Drinking Water Inspectorate Approvals are available for the inhibitor, biocide and polyelectroylte/coagulants used.

The present invention provides a composition for treating water systems, said composition comprising a corrosion inhibitor, a biocide and a flocculent.

Generally, the biocide may be any chlorine dioxide based biocide. One particularly convenient biocide is stabilised chlorine dioxide, which is a buffered solution of chlorine dioxide gas in an aqueous system. Normally simple salts, such as sodium carbonate, are included to provide the buffering effect. The

solubility of chlorine dioxide in aqueous media is low and generally solutions higher than 5% (weight:volume) cannot normally be achieved. Any concentration of stabilised chlorine dioxide may be used in the present invention, but particular mention may be made of 2%-5% (weight:volume) concentration in the composition. The pH of the stabilised chlorine dioxide solution may be adjusted as required. For example a pH of from 7 to 10, especially 7-7.5 up to 9-9.5 may be suitable. Commercially available stabilised chlorine dioxide solutions are available, such as BIOX™ from Viscona and PURAGENE™ from Vernacare. Optionally 20-30 ppm, especially approximately 25 ppm of chlorine dioxide should be generated during sterilisation procedures.

Any chlorine dioxide may be neutralised, for example with sodium thiosulphate, prior to drainage.

An advantage of using a chlorine dioxide based biocide is its ability to strip biofilm, the deposit of bacteria which adheres to the internal surface of pipes etc.

Generally, the corrosion inhibitor may be a polysilicate, especially a polysilicate salt such as sodium polysilicate. Suitable quantities of polysilicate or polysilicate salt in the composition include an aqueous solution of up to 30% (weight:volume). However concentrations of less than this, for example about 8 to 15% by weight:volume may be suitable for certain systems.

Other additives, including hydroxyethylene diphosphonate (HEDP), methylenebenzyltriazole (MBT) and/or polyacrylates (from a commercial source) may also be present, if required. Advantageously a

polysilicate corrosion inhibitor may be used in combination with a polyacrylate. Generally the silicate level in the treated water system will be in the region of from 20 ppm to 100 ppm, preferably 40 ppm to 60 ppm.

However, any material which acts to keep the biocide in a dispersed form may be acceptable.

The flocculant may be a polyelectrolyte (alternatively termed a "mud mover"). Such additives are known in the art and are used to flocculate solid material, thus keeping metal surfaces clean. Examples of suitable polyelectrolytes include polyacrylamides. Depending upon the system if the polyacrylamides chosen may be anionic, non-ionic or cationic. Especially suitable anionic polyacrylamides include those of low charge and with a molecular weight of 5-50kDa, especially 15-25kDa.

Suitable non-ionic polyacrylamides may be of a molecular weight of 5-50kDa, especially 15-25kDa. Suitable cationic polyacrylates include those of high charge and with a high molecular weight, for example over 50kDa.

The combination of polysilicates and polyelectrolytes has surprising advantages and gives a general corrosion rate of less than 5 mpy with no pitting.

The use of a flocculant in the composition of the present invention enables the stripped biofilm to be completely removed and flushed from the system.

The present invention further provides the use of a composition containing a corrosion inhibitor a biocide

and a flocculant for cleaning, and preferably sterilising, a water system.

Further, the present invention provides a method of cleaning (and disinfecting) a water system, said method comprising the addition of a corrosion inhibitor, a biocide and a flocculant to said system. It is not necessary that all the active ingredients are added together, although in certain applications that may be desirable. Thus in some situations it may be acceptable to add the ingredients sequentially.

In a further aspect, the present invention provides a kit for cleaning water systems, said kit comprising:

a) a corrosion inhibitor;
b) a biocide; and
c) a flocculant

wherein optionally at least one of the components listed above is packaged separately.

In a further aspect, the present invention provides the use of a corrosion inhibitor in the manufacture of a composition according to the present inhibitor.

In a further aspect, the present invention provides the use of a biocide in the manufacture of a composition according to the present inhibitor.

In a further aspect, the present invention provides the use of a flocculant in the manufacture of a composition according to the present invention.

We do not consider that the techniques and chemicals which are used at present and are advocated by the

Health and Safety Executive can guarantee the elimination of Legionella risk from cooling water systems. Work has indicated that the biocides currently used, and particularly the halogens, will not penetrate biofilm or destroy the amoeba which can act as host for the Legionella bacterium. CAMR have for instance reported that a bromine level of 8 mg/l had no effect on Legionella hidden in a surface biofilm and work at Sheffield (Hallam) University has indicated the failure of chlorine to kill host Amoeba when used at levels recommended by HS(G)70.

It is also the experience of the water treatment companies and cooling tower operators that following the recommendations of HS(G)70 does not necessarily prevent proliferation of Legionella bacteria. The complexity of cooling water systems, the variety of different materials and the possibility of amoeba and biofilm hideout means that current thoughts on acceptable biocides may not be valid.

We believe that chlorine dioxide is a fundamental ingredient of any water treatment which claims to be effective against Legionella. There is already a body of practical information available to suggest that chlorine dioxide can penetrate and remove biofilm. On many occasions large quantities of biofilm have been removed from systems which had been recently disinfected with chlorine. This will be the claim of many operators who routinely use chlorine dioxide for sterilisations or for those who have been asked to perform a sterilisation on a cooling tower which has been routinely disinfected using hypochlorite solution and is disinfected for the first time using chlorine dioxide. It is one of the underlying claims of the Liverpool Broadgreen Hospital report where chlorine

dioxide replaced bleach as the biocide and removed the Legionella risk from the hospital hot water systems which had been the cause of recurring Legionella problems while operating on a chlorine based regime.

Chlorine dioxide has found little application as a cooling water treatment biocide in the past and there have been good reasons for this.

1. Almost all of the chlorine dioxide used for water treatment was produced using generators. Generators got themselves a bad reputation in the past as some of the early ones were poorly made and managed to blow themselves apart. Chlorine dioxide generators represent a fair capital investment which would not be considered appropriate for many small and medium sized cooling water systems.

2. Chlorine dioxide cannot be transported and must be produced on site. This involves the handling of chemicals which would be considered as hazardous.

3. While much is known about chlorine dioxide as a disinfectant in the potable water treatment industry little is known about it as a cooling water biocide. There are in fact few bacterial and viral strains against which chlorine dioxide is not completely effective.

4. The advent of stabilised chlorine dioxide to this country is relatively recent and all the major water treatment companies have decided not to add it to their product portfolio at present. This is a decision which they will almost certainly revoke as information on the effectiveness of these

products becomes more widespread.

5. Stabilised chlorine dioxide has been compared unfairly with bleach (14.5% free chlorine) as a disinfectant in situations where it is used as a direct replacement. If it is assumed that bleach can be sold for around £0.35/litre and chlorine dioxide is 7 times more efficient than chlorine then a 2% chlorine dioxide solution should be roughly the same price, ie £0.35/litre. In fact the price will be roughly 10 times this and one of the greatest hurdles which stabilised chlorine dioxide will have to leap is this invidious price comparison with bleach. The material cost competes well with the other commonly used biocides.

It is clear from the more recent outbreaks of Legionnaire's Disease that a new product needs to be used as the standard disinfectant in water systems, and in particular the more complex cooling water systems. We believe that this need is fulfilled by the composition of the present invention.

The value of a thorough clean and disinfection using chlorine dioxide should not be understated. If a system can be brought to a condition of "industrial sterility" then ongoing treatment becomes straightforward and relatively non problematic.

People require to change their thinking about the importance of the seasonal disinfection. It is not something that is done twice per annum as a microbiological purging of the system. It is something that is done to give the Delta PA treatment a firm foundation. Often after this first disinfection

microbiological control can be effected by dosing the stabilised chlorine dioxide based product without activation.

When the biofilm has been completely removed and it is only adventitious bacteria entering the system which need to be dealt with then the stabilised material can activate itself on the acidic cell wall of the bacterium releasing the chlorine dioxide will kill the bug.

This sort of situation required careful monitoring and any sudden increases in microbiological population needs to be addressed by activating the product. The level of activation will depend on the type of system and the particular problem.

Some systems only need a shock dose perhaps once or twice per week to control the bug count, others may require a variation between of stabilised and activated chlorine dioxide.

A further constraint on dosing is that the DELTA PA Programme is being marketed as being environmental friendly and the ongoing treatment level should if possible be confined to 1 mg/l to 3 mg/l.

It is for this reason that the effectiveness of the disinfection is stressed. When it is conducted properly and the neutralisation of residual chlorine dioxide has been completed then the system should be controlled by low level dosing of the DELTA PA 6 range. Any sudden increase in the chlorine dioxide demand must be treated as an emergency situation requiring a mini on-line disinfection with neutralisation of any blowdown from the system.

EXAMPLE

While each cooling water system treatment regime is customised the treatment proposed uses three chemicals:

1. DELTA PA 4 — Series which are inhibitors based on sodium polysilicate

2. DELTA PA 6 — Series of biocides which are based on "BIOX" a stabilised chlorine dioxide product.

3. DELTA PA 8 — Series of flocculant materials.

The inhibitor and the flocculant are dosed in proportion to the make up water to the system. The concentration in the make up will depend on the concentration factor in the system but we would normally expect a silicate level of 20ppm to 30ppm. The flocculant is dosed at a level of 10ppm to 100ppm depending on the product used.

The biocide can be dosed in a variety of ways eg continuously, on a batch basis, or depending on circumstances both. The biocide be dosed in the activated or non-activated form but generally at a maximum level of 1 or 2ppm in the cooling water. At the use level none of the materials used can have an adverse effect on the stream which receives the blowdown water from the cooling water system.

Experimental work has shown:

1. The DELTA PA system achieves corrosion rates of <3 mpy and no pitting on mild steel. Corrosion rates on copper, copper alloys and stainless steel are

<1 mpy.

2. Metal surfaces are kept free from biofilm and surface debris. This improved heat transfer and therefore energy efficiency improves the overall performance of the cooling water system.

3. All of the chemicals used are used in the treatment of potable water, are all approved by the Drinking Water Inspectorate and therefore are of low toxicity. This has been confirmed by Microtox testing.

4. The treatment is more effective if started immediately after a clean and sterilisation of the cooling tower using chlorine dioxide and polymer. The DELTA PA 6 product is activated and dosed at a rate to give 20 ppm ClO_2 in the cooling water.

The DELTA PA 8 product is dosed to ensure that biofilm and debris removed by the clean are dispersed and flocculated suitable for removal from the system. The unused chlorine dioxide in the waste water from the clean is treated with sodium thiosulphate or hydrogen peroxide prior to discharge.

5. The DELTA PA system lends itself to chemical cleaning of critical heat exchangers fouled with biofilm and iron oxide by adding inhibited citric acid with the DELTA PA 6 and DELTA PA 8 product. These cleans can be conducted on or off line depending on circumstances.

The chemicals which comprise the range to date are therefore:

1 DELTA PA 400 Series inhibitors and scale control chemicals.

DELTA PA 441 polysilicate concentrate 29% SiO_2 dosed to give 10 to 30 ppm product in the system. This product is used for large systems.

DELTA PA 442 is a 1:1 dilution of this product and DELTA PA4410 is a 10:1 dilution of this product.

DELTA PA 450 polysilicate and multichemical formulation dosed to give 70 ppm to 100 ppm in the system. This chemical is used in multimetal systems where something more efficient than a basic polysilicate is preferred. It is less environmentally friendly than DELTA PA 441. This formulation is also available as a 5:1 dilution called DELTA PA 445.

DELTA PA 470 polymer and phosphonate for threshold effect scale inhibition. This is dosed at 25 ppm to 40 ppm. Available as DELTA PA 471 which is a 1:1 dilution of DELTA PA 4710 as a 10:1 dilution.

DELTA PA 6 Series biocides.

The biocides are based on stabilised chlorine dioxide and comprise DELTA PA 62 a (2% stabilised chlorine dioxide solution) and DELTA PA 65 (a 5% stabilised chlorine dioxide solution).

The formulations may contain biodegradable surfactants and are less highly buffered than the conventional products. The real value of these products is in the range of activation techniques which could be used.

DELTA PA 8 Series: Coagulants and polymers.

A full range of cationic organic coagulants based on organic materials (non aluminium) are included in the programme..

A full range of polyelectrolytes is included in the range although there is a core of three products representing cationic, non ionic and anionic products.

Anionic polymers are best suited to inorganic and inert debris, eg silt and sand, while a strong cationic polyelectrolyte is best suited to oily deposits and organic debris.

We believe that the incorporation of chlorine dioxide into the microbiological control package is fundamental to Legionella control because the PA 6 series of biocides offers something that other commonly used biocides do not.

CLAIMS

1. A composition for treating water systems, said composition comprising a corrosion inhibitor, a biocide and a flocculant.

2. A composition as claimed in Claim 1 wherein said biocide is based on chlorine dioxide.

3. A composition as claimed in Claim 2 wherein said biocide is a buffered solution of chlorine dioxide gas in an aqueous system.

4. A composition as claimed in either one of Claims 2 and 3 wherein the concentration of chlorine dioxide is 2% to 5% (weight : volume).

5. A composition as claimed in any one of Claims 1 to 4 wherein said corrosion inhibitor is a polysilicate.

6. A composition as claimed in Claim 5 where the concentration of polysilicate is up to 30% (weight : volume).

7. A composition as claimed in any one of Claims 1 to 6 wherein said flocculant is a polyacrylamide.

8. A composition as claimed in any one of Claims 1 to 7 which further comprises hydroxydiphosphonate (HEDP), methylenebenzyltriazole (MBT) and/or polyacrylates.

9. Use of a composition as claimed in any one of Claims 1 to 8 for cleaning a water system.

10. A method of cleaning a water system, said method comprising the addition of a corrosion inhibitor, a biocide and a flocculant to said system.

11. A kit for cleaning water systems, said kit comprising:

a) a corrosion inhibitor;
b) a biocide; and
c) a flocculant

wherein optionally at least one of the components listed above is packaged separately.

12. A composition for treating water systems substantially as defined in the Example.

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The Patent Office

Application No: GB 9510498.0
Claims searched: 1-12

Examiner: Diane Davies
Date of search: 9 August 1995

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.N): C1C

Int Cl (Ed.6): C02F

Other: Online databases: EDOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB 2126579 A	(Buckman Labs Inc.) Ammonium salts which act as flocculants, mircrobiocides and corrosion inhibitors.	1
X	US 4790943 A	(SE Water Conservation Systems Inc) Treatment of waste water with biocide and flocculants	1-12
X	DE 2520360 A	(Wabag Wasserreinig) Use of oxidant and flocculant to purify and sterilise water from swimming pools.	1-12
X	GB 1381673 A	(J. O'Shea *et al*) A method of chemical treatment of water supplies, see in particular the list of chemicals on page 3.	1-12

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
& Member of the same patent family
A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.